

AMENDMENTS TO THE CLAIMS

1. (Currently amended) A time-temperature indicator for indicating a temperature change over time, comprising:

(a) at least one indicator compound selected from the group consisting of a diarylethene compound and a spiroaromatic compound in a first isomeric form, which is converted into a second isomeric form of said indicator compound in a valence isomerization reaction without migration of an atom or chemical group attached to said indicator compound in a time and temperature dependent manner, wherein the formation of the second isomeric form is detectable by monitoring a physical characteristic of the first isomeric form or the second isomeric form of the indicator, and

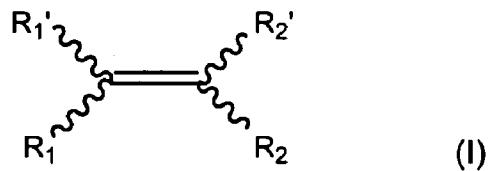
(c) a color filter that substantially filters out only the wavelength ranges causing undesirable renewed coloration of the indicator after the time-temperature clock has started

~~(b) a reference scale for evaluating the degree of decoloration or coloration, and~~

~~(e) a protector that prevents renewed photo-induced coloration of the indicator.~~

2. (Canceled)

3. (Previously presented) The time-temperature indicator of claim 1, wherein the diarylethene is a compound of Formula (I)



wherein:

R₁ and R₂ each independently represent C6-C14 aryl, C4-C12 heteroaryl, conjugated heterocyclic; wherein said heteroaryl and conjugated heterocyclic may contain one to three heteroatoms selected from the group consisting of N, O, and S; and wherein said aryl, heteroaryl, or conjugated heterocyclic may be substituted by one or more halogen, hydroxyl, thiol, amino, C1-C12 alkyl, C2-C12 alkenyl, C2-C12 alkynyl, C1-C6 alkanoyl, C1-C6 alkoxy, C1-C6

alkylthio, C6-C14 aryl, C4-C14 heteroaryl, C3-C8 membered non-aromatic carbocyclic, C3-C8 membered ring non-aromatic heterocyclic, cyano, nitro, sulfo, -CH=CH-CN, azido, or amido;

R₁' and R₂' each independently represent H, cyano, nitro, sulfo, hydroxyl, thiol, -CH=CH-CN, or amido; or substituted or unsubstituted C1-C12 alkyl, C2-C12 alkenyl, C2-C12 alkynyl, C1-C6 alkanoyl, C1-C6 alkoxy, C1-C6 alkylthio, C6-C14 aryl, C4-C14 heteroaryl, C3-C8 membered non-aromatic carbocyclic, C3-C8 membered ring non-aromatic heterocyclic; or R₁' and R₂' together with the carbon atoms to which they are attached form a C5-C8 carbocyclic ring or a C4-C7 heterocyclic ring containing one to three endocyclic or exocyclic heteroatoms selected from the group consisting of N, O, and S; said N heteroatom may be further substituted by H, or by one or two substituted or unsubstituted groups selected from the group consisting of C1-C12 alkyl, C2-C12 alkenyl, C2-C12 alkynyl, C1-C6 alkanoyl, C1-C6 alkoxy, C1-C6 alkylthio, C6-C14 aryl, C4-C14 heteroaryl, C3-C8 membered non-aromatic carbocyclic, C3-C8 membered ring non-aromatic heterocyclic, hydroxyl, and -CH=CH-CN; when said N heteroatom is tetrasubstituted it is positively charged and is associated with an anion selected from the group consisting of organic and inorganic anions, and optionally wherein said C5-C8 carbocycle is substituted by one or more halogen; and optionally

R₁, R₁', R₂ and R₂' each independently represent a charged group or a group substituted by another group having a charge; said charge may be localized or delocalized and may be positive or negative;

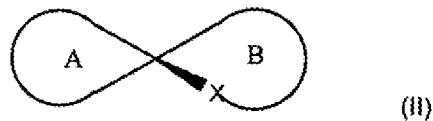
and wherein said R₁ and R₂ are in a cis or trans conformation.

4. (Previously presented) The time-temperature indicator of claim 3, wherein the diarylethene is

- (a) a symmetric diarylethene selected from the group consisting of 1,2-dicyano-1,2-bis(2,4,5-trimethylthiophene-3-yl)ethane (1); 2,3-bis(2,4,5-trimethylthiophene-3-yl)maleic anhydride (2); 1,2-bis(2-cyano-1,5-dimethyl-4-pyrrolyl)perfluorocyclopentene (3); and 1,2-bis(2,4-dimethyl-5-phenylthiophene-3-yl)perfluorocyclopentene (4); or

(b) an asymmetric diarylethene selected from the group consisting of 2-(1,2-dimethyl-3-indolyl)-3-(2,4,5-trimethyl-3-thienyl) maleic anhydride (5); and 2-(methoxybenzo[b]thiophene-3-yl)-3-(1,2-dimethyl-3-indolyl) maleic anhydride (6).

5. (Previously presented) The time-temperature indicator of claim 1, wherein the spiroaromatic compound is a compound of Formula (II):



wherein:

ring A represents a C5-C8 carbocycle, C4-C7 heterocycle containing at least one heteroatom selected from the group consisting of N, O, and S; said N heteroatom may be further substituted by one or two groups selected from the group consisting of C1-C12 alkyl, C2-C12 alkenyl, C2-C12 alkynyl, C1-C6 alkanoyl, C1-C6 alkoxy, C1-C6 alkylthio, C6-C14 aryl, C4-C14 heteroaryl, C3-C8 membered non-aromatic carbocyclic, C3-C8 membered ring non-aromatic heterocyclic, hydroxyl, and -CH=CH-CN; when said N heteroatom is tetrasubstituted it is positively charged and is associated with an anion selected from the group consisting of organic and inorganic anions; said C5-C8 carbocycle or C4-C7 heterocycle may be substituted by one or more of the groups selected from the group consisting of halogen, C1-C12 alkyl, C2-C12 alkenyl, C2-C12 alkynyl, C1-C6 alkanoyl, C1-C6 alkoxy, C1-C6 alkylthio, C6-C14 aryl, C4-C14 heteroaryl, C3-C8 membered non-aromatic carbocyclic, C3-C8 membered ring non-aromatic heterocyclic, cyano, nitro, sulfo, hydroxyl, thiol, -CH=CH-CN, azido, amido and amino;

ring B represents a substituted or unsubstituted heterocycle containing at least one heteroatom X, said X being selected from the group consisting of N, O, and S; wherein said N atom may be further substituted by one or two groups selected from the group consisting of C1-C12 alkyl, C2-C12 alkenyl, C2-C12 alkynyl, C1-C6 alkanoyl, C1-C6 alkoxy, C1-C6 alkylthio, C6-C14 aryl, C4-C14 heteroaryl, C3-C8 membered non-aromatic carbocyclic, C3-C8 membered ring

non-aromatic heterocyclic, hydroxyl, and CH=CH-CN; when said N heteroatom is tetrasubstituted it is positively charged and is associated with an anion selected from the group consisting of organic and inorganic anions;

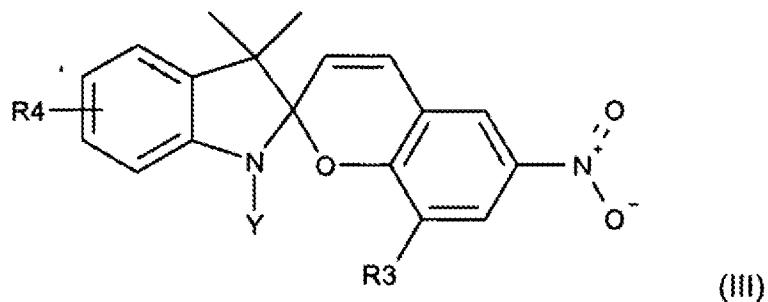
and wherein said ring B may contain one or more endocyclic double bonds and is optionally substituted by one or more halogen;

said rings A and B may be fused to one or more substituted or unsubstituted carbocycle, C4-C14 heterocycle, C6-C14 aryl or C4-C14 heteroaryl ring system;

and wherein the compounds of Formula (II) may be neutral, charged, multiply charged, positively charged having an external anion, negatively charged having an external cation or zwitterionic.

6. (Previously presented) The time-temperature indicator of claim 5, wherein the spiroaromatic compound is a spiropyran derivative.

7. (Previously presented) The time-temperature indicator of claim 5, wherein the spiropyran derivative is a derivative of 1',3',3'-trimethyl-6-nitro-spiro(2H-1-benzopyran-2,2'-2H-indole) of Formula (III):



wherein:

R3 is selected from the group consisting of H, halogen, C1-C12 alkyl, C2-C12 alkenyl, C2-C12 alkynyl, C1-C6 alkanoyl, C1-C6 alkoxy, C1-C6 alkylthio, C6-C14 aryl, C4-C14 heteroaryl, C3-C8 membered non-aromatic carbocyclic, C3-C8 membered ring non-aromatic heterocyclic, and azido; wherein said alkyl, alkenyl, alkynyl, aryl, heteroaryl, and non-aromatic carbocycle

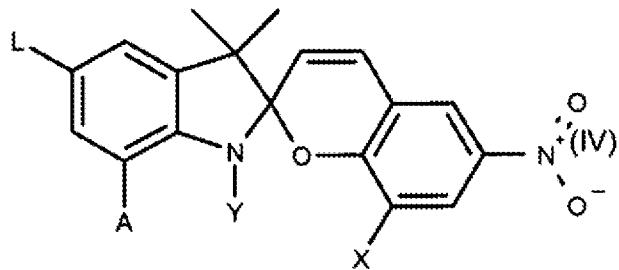
may be substituted by one or more group selected from the group consisting of halogen, hydroxyl, thiol, amino, alkoxy, nitro, azido, and sulfo;

R4 is selected from the group consisting of C1-C12 alkyl, C2-C12 alkenyl, C2-C12 alkynyl, C1-C6 alkanoyl, C1-C6 alkoxy, C1-C6 alkylthio, C6-C14 aryl, C4-C14 heteroaryl, C3-C8 membered non-aromatic carbocyclic, C3-C8 membered ring non-aromatic heterocyclic, hydroxyl and -CH=CH-CN; and

Y is selected from the group consisting of C1-C25 alkyl and C7-C15 aralkyl, wherein said alkyl and aralkyl is optionally substituted by one or more halogen.

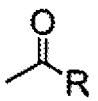
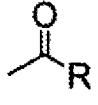
8. (Previously presented) The time-temperature indicator of claim 5, wherein the spiroaromatic compounds include at least one of the following: spirooxazine or its derivatives, spironaphthoxazine or its derivatives, and spiroindolinopyridobenzoxazine or its derivatives.

9. (Withdrawn) The time-temperature indicator of claim 1, wherein the spiroaromatic compound is a compound of Formula (IV):



wherein:

A and L are independently of each other selected from the group consisting of H, halogen,

C2-C12 alkenyl, C2-C12 alkynyl and , wherein R is C1-C6 alkyl, C1-C6 alkoxy, C6-C14 aryl and C7-C15 aralkyl; wherein said alkenyl, alkynyl and , may be substituted by one or

more groups selected from the group consisting of halogen, hydroxyl, thiol, amino, alkoxy, nitro, azido, sulfo, aryl and heteroaryl;

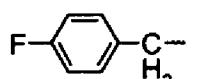
Y is selected from the group consisting of C1-C25 alkyl and C7-C15 aralkyl, wherein said alkyl and aralkyl is optionally substituted by one or more halogen; and

X is C1-C6 alkoxy or L;

with the proviso that Y is not n-propyl when L, A and X are hydrogen.

10. (Withdrawn) The time-temperature indicator of claim 9, wherein

L is hydrogen, Cl, Br or I;



Y is methyl, n-propyl, n-octadecyl or

X is hydrogen or methoxy; and

A is hydrogen;

with the proviso that Y is not n-propyl when L and X are hydrogen.

11. (Withdrawn) A printing ink or printing ink concentrate, comprising the time-temperature indicator of claim 9.

12. (Withdrawn) A high molecular weight material, comprising the time-temperature indicator of claim 9.

13. (Currently amended) A method of manufacturing the time-temperature indicator of claim 1, comprising the steps of

(a) embedding in or atop a matrix at least one indicator compound selected from the group consisting of a diarylethene compound and a spiroaromatic compound;

(b) inducing the formation of a metastable state of said embedded indicator compound; and

(c) covering the time-temperature indicator with a color filter that substantially filters out only the wavelength ranges causing undesirable renewed coloration of the indicator after

the time-temperature clock has started~~protector that prevents renewed photo induced coloration of the indicator.~~

14. (Cancelled)

15. (Previously presented) The time-temperature indicator of claim 6, wherein the spiropyran derivative is selected from the group consisting of 1',3',3',8-tetramethyl-5-hydroxymethyl-spiro(2H-pyrano[2,3-c]pyridine-2,2'-2H-indole) and 1',3',3',8-tetramethyl-spiro(2H-pyrano[2,3-c]pyridine-2,2'-2H-indole).

16. (Previously presented) The time-temperature indicator of claim 7, wherein in Formula (III) Y is selected from the group consisting of C1-C25 alkyl and C7-C15 aralkyl, wherein said alkyl and aralkyl are substituted by one or more fluorine.

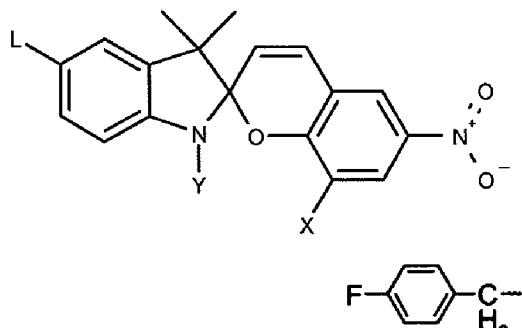
17. (Withdrawn) The time-temperature indicator of claim 9, wherein in Formula (IV) Y is selected from the group consisting of C1-C25 alkyl and C7-C15 aralkyl, wherein said alkyl and aralkyl are substituted by one or more fluorine.

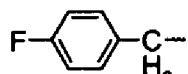
18. (Withdrawn) A printing ink or printing ink concentrate, comprising the time-temperature indicator of claim 10.

19. (Withdrawn) A high molecular weight material, comprising the time-temperature indicator of claim 10.

20. (Cancelled)

21. (Previously presented) The time-temperature indicator of claim 1, wherein the spiroaromatic compound has the formula



wherein L is hydrogen, Y is  and X is methoxy.

22. (Withdrawn-Currently amended) A packaging material or a label that comprises a time-temperature indicator for indicating a temperature change over time, comprising:

(a) at least one indicator compound selected from the group consisting of a diarylethene compound and a spiroaromatic compound in a first isomeric form, which is converted into a second isomeric form of said indicator compound in a valence isomerization reaction without migration of an atom or chemical group attached to said indicator compound in a time and temperature dependent manner, wherein the formation of the second isomeric form is detectable by monitoring a physical characteristic of the first isomeric or the second isomeric form of the indicator, and

(c) a color filter that substantially filters out only the wavelength ranges causing undesirable renewed coloration of the indicator after the time-temperature clock has started

(b) a reference scale or reference color for evaluating the degree of decoloration or coloration, and

(e) a protector that prevents renewed photo-induced coloration of the indicator to avoid photo recharging or photo bleaching.

23. (Previously presented) The time-temperature indicator of claim 3, wherein R₁' and R₂' together with the carbon atoms to which they are attached form a C5-C8 carbocyclic ring, wherein the C5-C8 carbocyclic ring is substituted by one or more fluorine atoms.

24. (New) The time-temperature indicator of claim 1, further comprising a reference scale for evaluating the degree of decoloration or coloration.

25. (New) The time-temperature indicator of claim 24, wherein the reference scale is a reference color.

26. (New) The time-temperature indicator of claim 1, wherein the at least one indicator compound is present in a crystalline form.